PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES **INDIA** 1946

PARTS V & VI]

Part III, Determination of e/m

of Specific charge of Li +

SECTION A

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ALLAHABAD

By B. N. Srivastava & A. S. Bhatnagar

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India): Rs. 5/8 (Foreign)

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SECTION A

[Vol. 15

THE EFFECT OF SPACE CHARGE ON ELECTRONIC CURRENTS: PART III, DETERMINATION OF e/m.

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1. Introduction

In Part I (Srivastava and Bhatnagar, 1944 a) we discussed theoretically the effect of space charge on electronic currents in the simple case where the electron beam is that effusing out of a narrow aperture in a heated graphite chamber, and the beam is limited to a cone of small angle with the help of a hole in a suitably placed metallic diaphragm. The electrons are collected in a Faraday cylinder which serves as the anode, to which various potentials can be applied, while the limiting diaphragm, which is electrically connected to the graphite tube, serves as the cathode. The analysis was given on the assumption that the angle of the cone, as limited by the diaphragm, is so small that the electronic beam issuing out of the diaphragm may be regarded as approximating to a parallel beam. In Part II (Srivastava and Bhatnagar, 1944 b) the dependence of the electronic current on the anode voltage was investigated experimentally and was found to agree within the limits of experimental

error with the results deduced theoretically in paper I (see Table IV of paper II).

A very useful and interesting feature of these investigations is the dependence of the current i on the anode voltage V as expressed by the approximate equation (24) of Part I, which is valid for large values of η . This is

$$i = \frac{\sqrt{2}}{9\pi} \left(\frac{e}{m}\right)^{1/2} \frac{(V - V_m)^{3/2} A}{(x - x_m)^2} \left[1 + \frac{3}{4} \frac{3 + 2P}{1 + P} \sqrt{\frac{\pi}{\eta}}\right]. \tag{1}$$

It was shown in Paper II that on plotting $i^{2/3}$ against V a straight line is obtained (see Fig. 1 of Paper II) even for low values of V and the slope of this straight line was utilised for the calculation of e/m. This mode of calculation will be justifiable if x_m and the second term in the square bracket [] is negligible, and V_m is either constant or negligible. Since this method furnishes a simple but important method of identifying the charged particles which is likely to prove of great utility, it is necessary to examine critically the steps leading on to equation (1) with a view to discover what deviations may be expected from it, and also to investigate the effect of x_m , V_m and the second term inside the square bracket on the value of e/m calculated by this method. This we propose to do in the present paper.

2. Derivation of Equation (1) and the so-called Child's Approximation

The function $\phi(\eta)$ expressed by I (22) was expanded by using an asymptotic expansion for erf $\sqrt{\eta}$ for large values of $\sqrt{\eta}$. Since $\sqrt{\eta}$ under the conditions of the experiment (vol age range 0.2 to 2.5 volts) varies from about 2 to 4, only the first two terms in the asymptotic expansion

$$e^{\eta} (1 - \operatorname{erf} \sqrt{\eta}) = \frac{1}{\sqrt{\pi \eta}} \left[1 - \frac{1}{2\eta} + \frac{1 \cdot 3}{(2\eta)^2} - \frac{1 \cdot 3 \cdot 5}{(2\eta)^3} + \dots \right]$$

need be retained and the error involved in stopping at the second term is seen to be small and negligible. Substituting this value in

I (23) and developing into a series expansion and retaining only two terms we get

 $\xi^{2} = \frac{4}{9} \frac{\pi^{1/2} \eta^{3/2}}{1+P} \left[1 + \frac{3}{4} \frac{3+2P}{1+P} \sqrt{\frac{\pi}{n}} \right]. \tag{2}$

The higher powers of $\eta^{-1/2}$ are neglected in view of the fact that only two terms were retained in the expansion of erf $\sqrt{\eta}$. In view of these approximations it is desirable to test the validity of equation (2) by actually comparing the values of ξ obtained for different values of η from equation (2) with those obtained from numerical integration of I (23) for the same values of η , the latter values being given in table III of paper II. Thus taking $P=2\cdot289$, equation (2) gives for $\eta=3$, 5, 7, 15, 20 the ξ -values $1\cdot856$, $2\cdot519$, $3\cdot093$, $4\cdot991$, $6\cdot008$ respectively, while the respective values obtained by numerical integration are $1\cdot828$, $2\cdot484$, $3\cdot051$, $4\cdot914$ and $5\cdot915$. It is therefore seen that equation (2) gives the values of ξ correct to about 2% in the desired range of values of η . Hence for all practical purposes its validity is established. Substituting this value of ξ^2 in I (18) we get equation (1) which is thus seen to be correct to about 4%.

Though equation (1) shows a formal resemblance with Child's equation, it differs from the latter in one important respect, viz. it involves the quantity $V - V_m$ in place of V. The consequence of this is that the plot of $i^{2/3}$ against V intersects the ordinate for V = 0 not at $i^{2/3} = 0$ as would occur if Child's equation were to hold, (see Fig. 1 of paper II) but at some positive value of $i^{2/3}$ (say $i_0^{2/3}$), so that i = 0 will algebraically correspond to a negative value of V which will be equal to V_m . From the figure V_m comes out to be -36 volts which thus represents the mean value of V_m in the region under consideration as V_m actually varies with V.

To test equation (1) fully we must know the values of V_m , and x_m . This was already given in table IV of Paper II. We must however know the value of A.

3. VALUE OF A

We have developed the space charge theory for a parallel beam of charged particles. Even if the effusion hole and the hole in the limiting diaphragm are of the same size, there will be regions of umbra and penumbra, as in optics, and the beam will not be perfectly parallel. The penumbral intensity will however be much less. In the actual experiments the beam is also slightly divergent and this will cause a further departure from parallelism. The accelerating electrical field, on the other hand, increases the forward velocity and thereby decreases this tendency towards departure from parallelism. An approximate calculation may be made to show the order of magnitude of these effects.

For the data given in table IV of paper II, r_E , the radius of the effusion hole = 0.09 cm, r_D , the radius of the hole in the limiting diaphragm = 0.15 cm, distance of diaphragm from effusion hole = 2.1 cm, distance of anode from diaphragm (cathode) = 2.4 cm. Simple geometry shows that in the absence of the electrical field, neglecting the small lateral spreading of the electrons due to mutual repulsion, the outer radius of the umbral region = 0.22 cm, (Fig. 1) and that of

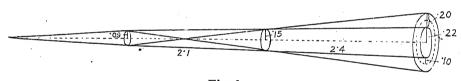


Fig. 1.

the penumbral region = 0.42 cm. The intensity over the greater part of the penumbral region is however much less, and goes on decreasing as the periphery of the penumbra is approached. Detailed considerations show that the penumbra will have the same total intensity as a circle of outer radius about 0.32 cm. having the same intensity as the umbra, provided we neglect the somewhat more rapid fall of intensity in the penumbra towards the periphery produced by the increased obliquity and the slightly increased distance. The effective area will therefore be still less.

The effect of the electrical field in decreasing this spreading of the beam can be calculated as follows:—

An electron of velocity c traversing in a direction inclined to the forward direction by an angle θ suffers an acceleration = Ee/m in the forward direction where E is the electrical field. The time t, taken in traversing the distance a between the electric under the action of the field is given by

$$a = t c \cos \theta + \frac{1}{2} \frac{Ee}{m} t^2. \tag{3}$$

Hence

$$t = -\frac{mc}{Ee} \cos \theta + \sqrt{\frac{m^2c^2}{E^2e^2}\cos^2 \theta + \frac{2m}{Ee}a}. \qquad (4)$$

The vertical displacement is now not a tan θ as would have been in the absence of the field but is equal to $tc\sin\theta$. The displacement thus becomes decreased by the etectrical field in the ratio

$$\frac{c t \sin \theta}{a \tan \theta} = \frac{c}{a} \cos \theta + \left[-\frac{mc}{Ee} \cos \theta + \sqrt{\frac{m^2 c^2}{E^2 e^2} \cos^2 \theta + \frac{2m}{Ee}} a \right] . \qquad (5)$$

It is thus seen to depend upon c, θ and E. Calculation of the average value requires integration over all values of c and over all admissible values of θ . Further this average value will be different for different values of E, which shows that the effective A will depend upon E. Thus A is not constant for different applied voltages and therefore no useful purpose will be served by calculating an average value of the ratio expressed by (5) for all values of c and θ .

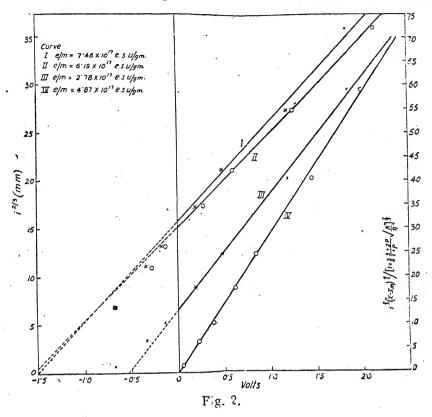
In order to obtain an idea of the numerical magnitudes involved we shall calculate the ratio expressed by (5) for the most probable velocity α in the emitted beam which is equal to $\sqrt{(3kT/m)}$. Assuming $T=1863^\circ$ K, $a=2\cdot4$ cm, $E=\frac{1\cdot5}{2\cdot4}$ volt/cm, $\cos\theta=1$, the ratio (5) for the most probable velocity comes out to be 0.54. Of course it varies with E the applied field. The most probable value for the penumbral radius = $\cdot32 \times \cdot54 = \cdot17$ cm. for this particular field. Due to the elect-

rical field the umbral radius will also be reduced. Working on the same basis as for the penumbra above, the radius of the umbra will be .09+ $(.22 - .09) \times .54 = .16$ cm, while the radius of the limiting diaphragm is .15 Thus the mean radius of the beam cross-section = $\frac{1}{2}$ (15+17) = ·16 and differs from the radius of the diaphragm by about 7%. This cross-section will vary with the applied voltage. More exact calculation is not considered worthwhile because the space-charge theory as developed in paper I applies essentially to a parallel beam and will require considerable modification if we want to take into account any presence of divergence in the beam. The foregoing calculations serve to show that (1) the beam cross-section will certainly be somewhat greater than the area of the limiting hole, (2) the error committed in assuming the area of the hole to represent the beam cross-section may not exceed 15%. In view of the approximate nature of the foregoing calculations for the average beam cross section which will not be the same for different applied voltages, we shall hereafter assume this A to be equal to the area of the limiting hole, but the result is liable to an error of about 15%.

4. Testing of Equation (1)

Substituting in equation (1) the values of V_m and x_m given in table IV of paper II for the anode voltages 1.85, 1.19 and 0.48 volts respectively and taking A to be equal to the area of the limiting hole (=0.0707 sq. cm.) the values of i found for these anode voltages are 222×10^{-9} , 163×10^{-9} and 100×10^{-9} amperes respectively. The experimentally observed values are 215.6×10^{-9} , 143.7×10^{-9} and 95.7×10^{-9} amperes respectively and this agreement should be considered sufficiently good in view of the possible errors in the assumed value of A and in the calculated values of V_m and x_m utilised in equation (1). Thus equation (1) is verified quantitatively. If we neglect V_m , x_m and the second term inside the bracket we obtain for V=1.85 volts, $i=72\times 10^{-9}$ amperes which shows that Child's approximation is totally wrong at these low voltages for the purpose of calculating the absolute value of i.

To show the effect of the terms x_m , V_m and the second term inside the brackets [] in equation (1) on the usual plot $i^{2/3}$ against



V, several curves are plotted in Fig. 2 from the data given in table IV of paper II. Curves I and II represent the plot of $i^{2/3}$ against V and will be referred to as the uncorrected curves. In curve I the calculated anode voltage is used while in II the experimentally measured anode voltage is utilised. In curve III the quantity

$$i^{2/3} (x-x_m)^{4/3} / \left[1 + \frac{3}{4} \frac{3+2P}{1+P} \sqrt{\frac{\pi}{\eta}} \right]^{2/3}$$

is plotted against V while in curve IV this very quantity is plotted against $V-V_m$. It will be seen that the uncorrected curves I and II are approximately straight lines but their intercepts on the V-axis give the V_m values -1.5 and -1.56 volts while the average V_m values are much smaller numerically (see table IV). The

straight lines have been drawn on the basis of the four positive values only and the negative values have been disregarded because for the positive values alone the condition $\eta > 3$, which is necessary for the asymptotic expansion of erf $\sqrt{\eta}$ to hold and for equation (1) to be valid, is satisfied. The values of e/m calculated from the slope of the straight lines I and II from the relation

slope =
$$\left[\frac{\sqrt{2}}{9\pi} \left(\frac{e}{m}\right)^{1/2} \frac{A}{x^2}\right]^{2/3}$$
 (6)

are 7.46×10^{17} e.s. u./gm. and 6.19×10^{17} e.s.u./gm. respectively, which are a bit too high. The corrected curve III does not remain a straight line but bends at the lower end on account of the continuous variation of V_m but the different portions of the curve give intercepts agreeing with the observed values of V_m . The points in curve IV lie very well on a straight line passing through the origin with a slope which gives with the help of the relation

Slope =
$$\left[\frac{\sqrt{2}}{9\pi} \left(\frac{e}{m}\right)^{1/2} A\right]^{2/3}$$
, (7)

the value 4.87×10^{17} e.s.u./gm for e/m. This value agrees closely with the correct value 5.28 × 1017. Thus the superiority of the corrected curve IV over the uncorrected curves I and II is obvious from considerations of accuracy in e/m and V_m but as the former requires the values of V_m , x_m etc. it is often not practicable, since the calculation of x_m requires the knowledge of the mass of the particle. Therefore we have almost invariably to plot the uncorrected curve II from the observed experimental data. The reason why the uncorrected curve comes out to be approximately a straight line is that V_m , x_m and the Pterm, all vary only very slowly in the experimental range. Taking the actual data in Table IV it is found that the variation of the P term causes a variation in $i^{2/3}$ by about 6% on either side of some mean value, that of x_m by about 10% while that of V_m by about 10%. All these variations are in the same direction and therefore assist one another. Thus the variation in slope between the two extreme ends may be about 26% but over a very large range it is less than 15%. It is for this reason that the uncorrected plot (curve II) comes out to be approximately a straight line. The slope and the intercept i.e. e/m and V_m

calculated from this uncorrected plot will however not be correct on account of the non-vanishing average values of V_m , x_m and the P term. It will be noticed, however, that for these low voltages, though the approximate Child's equation gives values for i which are in error by as much as 300%, yet it gives an error of only about 20 to 40% in the calculated value of e/m. This arises from the following fortunate circumstance:— This method of calculating e/m does not actually assume Child's equation (for this would require us to calculate from the slope of the line formed by joining any point on the plot to the origin) but merely the observed rate of variation of the current with voltage over a limited range. If i and i_0 denote the currents for the anode voltages V and 0, then (1) gives

$$i^{2/3} = \frac{a(V - V_m)\alpha}{(x - x_m)^{4/3}}; \qquad i_{\circ}^{2/3} = -\frac{aV_{m,o}\alpha_o}{(x - x_m,o)^{4/3}},$$

$$a = \left[\frac{\sqrt{2}}{9\pi} \left(\frac{e}{m}\right)^{1/2} A\right]^{2/3},$$
(8)

where

$$\alpha = \left[\begin{array}{cc} 1 + \frac{3}{4} \frac{\left(3 - 2e\right)V_m/kT}{1 - eV_m/kT} & \sqrt{\frac{\pi}{e(V - V_m)/kT}} \end{array} \right]^{2/3}$$

$$\alpha_{o} = \left[1 + \frac{3}{4} \frac{3 - 2eV_{m,o}/kT}{1 - eV_{m,o}/kT} \sqrt{\frac{\pi}{-eV_{m,o}/kT}} \right]^{2/3}$$

and $V_{m,o}$ $x_{m,o}$ denote the values of V_m and x_m at zero anode voltage. From (8) we have

$$i^{2/3} - i_0^{2/3} = \frac{aV}{x^{4/3}} \left\{ \frac{(1 - V_m/V)\alpha}{(1 - x_m/x)^{4/3}} + \frac{\alpha_0 V_{mo}/V}{(1 - x_{mo}/x)^{4/3}} \right\}.$$
 (9)

For the data given in table IV of paper II we have :—for V=1.85 volts, $V_m=-.15$, $x_m=.38$ cm, $\alpha=(1.95)^{2/3}$, x=2.4 cm, and for V=0, $V_{m0}=-.47$ volts, $x_{m0}=.87$ cm, $\alpha_0=(2.75)^{2/3}$, $i_0=59.5\times10^{-9}$ amperes. Substituting these values in (9) we get the value of the bracket $\{ \}$ to be 1.21. Thus we can write

$$i^{2l^3} - i_0^{2l^3} \approx \frac{aV}{x^4/3},$$
 (10)

since the bracket $\{\}$ term is of the order unity. It is on account of the fact that (1) can be written in the form (10) that the plot of i^{2l^3} against V gives from its slope a/x^{4l^3} an approximately correct (actually slightly higher on account of the factor 1.21) value of e/m. We can also

use (8) to calculate e/m from the intercept $i_0^{2/3}$ and the calculated values of V_{mo} , x_{mo} and α_0 . This in the present case comes out to be $4.8 \times 10^{1.7}$ e.s.u./gm.

It will thus be seen that equation (1), though complicated by the presence of various factors, reduces to the form (10) and thereby furnishes us with a very simple practical method of determining e/m for charged particles.

SUMMARY

It has been established that the plot $i^{2/3}$ against V specially in the region of positive applied voltages is approximately a straight line whose slope gives e/m. The method, however, suffers from the limitation that the value of e/m obtained in this manner may be in error by as much as 20% or so. It is of value in identifying particles when the mass is known or in determining the nature of the particles from an approximate determination of mass but cannot be useful for an accurate determination of mass of the particles.

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Srivastava, B. N. and Bhatnagar, A. S., 1944a Proc. Nat. Acad. Sci. India, 14, 106. 1944b, Ibid, 14, 118.

THERMAL IONIZATION OF LITHIUM AND DETERMINATION OF SPECIFIC CHARGE OF Li⁺

By

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1. Introduction

The vacuum graphite furnace constructed by Saha and Tandon (1936) was first employed by Srivastava (1940 a, 1940 b) for studying the thermal ionization of barium and strontium. Later the elements sodium and potassium were studied by Bhatnagar (1943 a) by the same method. In these experiments the vapour of the element suffers ionization inside a heated graphite chamber and the products of ionization, viz., electrons and ions effuse out of a fine hole in the chamber and are collected by a Faraday cylinder to which a suitable voltage is applied. The currents produced by these charged particles are measured by a galvanometer, this being the most important part of the experiment. The procedure followed so far was to apply a sufficiently high voltage to the Faraday cylinder and measure the saturation current; the nature of the particles producing the currents was not examined.

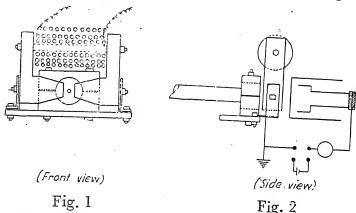
In the present work on lithium, the current has been measured at various voltages on the Faraday cylinder and from this by applying the space charge theory already developed (Srivastava and Bhatnagar 1944 a, 1944b), we can find e/m for the particles producing the current provided the current is unipolar (Srivastava 1946).

2. Determination of e/m

A theory of the space charge effect for the arrangement of electrodes used in our experiment has already been worked out in a previous paper by us (1944 a), which will be hereafter referred to as paper I.

There the theory was worked out for unipolar currents only. In the present case, however, the space between the electrodes contains particles having positive as well as negative charges. Therefore, this is a case of bipolar currents under various voltages. The theory for this case will evidently be more complicated as both types of ions (+ve and -ve) will contribute to the space charge. By the use of an electromagnet, however, it has been found possible to deflect away the negative particles consisting mainly of electrons and thereby obtain a positive unipolar current to which the theory already developed in part I will be applicable.

The arrangement of the apparatus is the same as in previous experiments except that a strong electromagnet in the form of a rectangle with a small clearance gap has been utilised to deflect the electrons more completely than hitherto. Fig. 1 shows the



electromagnet as viewed from the Faraday cylinder. Fig. 2 gives the side view, showing the relative arrangement of the electromagnet with respect to the graphite furnace and the Faraday cylinder. By passing a sufficient current through the electromagnet the electrons are completely prevented from reaching the Faraday cylinder whenever desired. The heavier ions are, however, not appreciably affected by this magnetic field.

A typical set of measurements of current at various voltages with

Table I

T = 1825°K	Galv. sens. = 1.25×10^{-9} amp/mm.
x = 2.4 cm.	$A = \pi \times (42)^2 \text{ sq. cm.}$

			11-11 × (42)-sq. cm.			
	d-in	ı mm.	d ⁺ in mm.			
Volts	Without mag. field	With mag. field	Without mag. field	With mag. field		
0	148	8	-148	-8		
•2	230	23	—15	6.5		
.4	280	27	-2	7•4		
•5	288	28	6	8.1		
.6	300	30	8.5	8.5		
1•0	410	42	10	9.8		
1.5	518	53	11.5	11.4		
2.0	649	67	14	13.8		
2.5	770	79	16	15•8		
3.0	810	83	18	18.0		
4.0	880	89	24	23.5		
5.0	995	100	27	26.8		

It is seen that a retarding potential of about 0.6 volts on the Faraday cylinder is sufficient to prevent completely the negative particles from reaching the Faraday cylinder. This will be evident by examining columns 4 and 5 of the Table. For voltages less than this

the application of the magnetic field causes an increase in the positive current which is to be attributed to the partial or total deflection of Above 0.6 volts the positive currents show no increase on the application of the magnetic field indicating thereby that no measurable number of electrons is able to overcome this retarding field and register themselves on the anode. From this, however, it does not follow that above 0.6 volts the space between the electrodes contains only the positive ions. As a matter of fact even at this voltage quite a large number of electrons must be entering the space between the electrodes and traversing some distance before being finally returned to the cathode. Hence, by the mere application of the retarding voltages (unless they are very high) it will not be justifiable to assume the existence of unipolar currents. The easiest way to obtain unipolar positive currents is to deflect the electrons by a magnetic field before they enter the space enclosed by the electrodes. This device, however, cannot be employed for obtaining a negative unipolar current since the positive ions are much less deflected than the electrons and so if the field is made strong enough it will cut off both of them.

In paper I, we obtained the relation

$$i = \frac{\sqrt{2}}{9\pi} \left(\frac{e}{m}\right)^{1/2} \frac{V^{3/2}}{x^2}.$$
 (1)

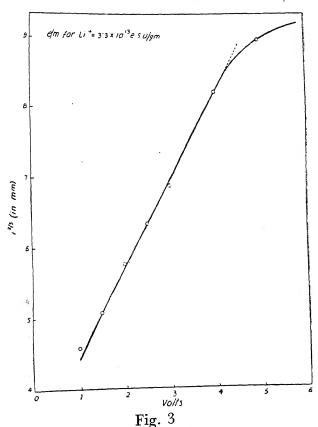
as an approximate form of

$$i = \frac{\sqrt{2}}{9\pi} \left(\frac{e}{m}\right)^{1/2} \frac{(V - V_m)^{3/2}}{(x - x_m)^2} A \left[1 + \frac{3}{4} \frac{3 + 2P}{1 + P} \sqrt{\frac{\pi}{\eta}} + \dots \right],$$

where A may be put equal to the area of the aperture in the diaphragm serving as cathode and x denotes the distance between the electrodes, viz., the diaphragm and the Faraday cylinder for our experimental arrangement. e/m refers to the particles producing the current i.

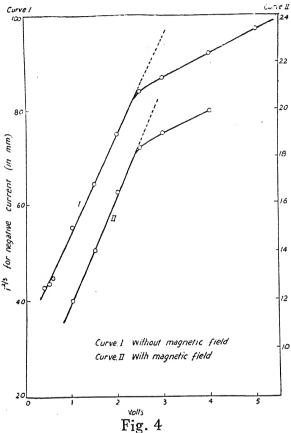
As explained above the positive current obtained by applying the magnetic field will be unipolar and hence equation (1) will be applicable to it. Plotting $i^{2/3}$ against V for the positive currents as given in column 5 of table I, we obtain the line shown in Fig. 3. A in the experiment was $\pi \times (0.42)^2$ sq. cm. and x = 2.4 cm, hence from

the slope of the line we obtain e/m for positive particles= 3.3×10^{13} e.s.u./gm. Taking $e=4.80\cdot 10^{-10}$ e.s.u. we obtain the mass of the positive ion to be 8.7 times the mass of the hydrogen atom, a value which agrees within about 25% with the value expected for Li⁺. The somewhat higher value obtained for m may be due to the greater divergence of the beam in the present investigations than that in paper II or to the presence of some fast negative particles (electrons) which do manage to enter the electrode space in spite of the magnetic field but are not able to reach the Faraday cylinder on account of the retarding voltage. In general these investigations too confirm the space charge theory and establish with certainty the nature of the positive ion.



It will be interesting to find how far equation (1) will be applicable to the negative current. Assuming for a moment that this equation holds for negative currents also, the observations given in

columns 1 and 2 of Table I have been plotted as $i^{2/3}$ against V (see curve I fig. 4) and the value of e/m for the negative particles has



been calculated and comes out to be 1.4×10^{17} e.s.u./gm. The value is of the same order as that for the electrons $(5.3 \times 10^{17} \text{ e.s.u/gm})$ showing that the negative particles consist mainly of electrons. The agreement evidently is poor, the value obtained being much less than that for a pure electron beam. There may be two reasons for this discrepancy: (1) either the theory of the unipolar current is not applicable to this case since positive particles are also present, or (2) there may be some heavier negative particles in addition to the electrons in the negative current which will cause the effective value of e/m for the electrons to be somewhat smaller than that for pure electrons. To examine this latter possibility further, it is necessary to obtain in

detail a theory of unipolar currents produced by a mixture of two types of particles with similar charges but different masses under different applied voltages. This requires some modification of the space charge theory already developed in paper I.

Poisson's equation gives
$$\nabla^2 V = -4\pi\rho, \qquad (2)$$

where, for this case $\rho = \rho_e + \rho_i$ the respective charge densities due to electrons and negative ions.

The potential distribution in space is established as a result of the presence of both types of particles, i. e., negative ions and electrons; but the number of negative ions, in the particular case we are considering, is very small and hence we can assume, as a first approximation, that its effect on the potential distribution is only very slight, and hence the general nature of the potential distribution is the same as that due to a unipolar unicomponent current. In particular we assume that a single potential minimum still exists between the electrodes. Evidently whatever potential distribution is established in the space it must be the same for both the types of particles. The value of dv/dx as obtained in paper I can, therefore, be easily substituted in equation (2) and we obtain for the α -region,

$$\left(\frac{\partial V}{\partial x}\right)^{2} = \frac{8\pi m_{e}}{A} \left[\int_{[2e(V_{1}-V_{m})/m_{e}]^{1/2}}^{\infty} \left[\int_{[2e(V_{1}-V_{m})/m_{e}]^{1/2}}^{\infty} \int_{[2e(V_{1}-V)/m_{e}]^{1/2}}^{2e(V_{1}-V_{m})/m_{e}]^{1/2}} \right] + \frac{8\pi m_{i}}{A} \left[\int_{[2e(V_{1}-V_{m})/m_{i}]^{1/2}}^{\infty} \int_{[2e(V_{1}-V_{m})/m_{i}]^{1/2}}^{2e(V_{1}-V_{m})/m_{i}]^{1/2}} \int_{[2e(V_{1}-V)/m_{i}]^{1/2}}^{2e(V_{1}-V_{m})/m_{i}]^{1/2}} \right] (3)$$

where n_e , m_e refer to the electrons and n_i , m_i to the negative ions.

For β -region the second term in both the square brackets is to be omitted. Integrating the right hand side of (3) we obtain

$$\left(\frac{\partial V}{\partial x}\right)^2 = \frac{S}{A} \sin^2 \theta_0 \ 2\pi k T \ \phi(\eta) \ [n_e + n_i] \ \varepsilon^{-p}, \tag{4}$$

since η and P do not depend upon the mass of the particles and are given by

 $\eta = \frac{e(V - V_m)}{kT}, P = \frac{e(V_1 - V_m)}{kT},$ and $\phi(\eta) - \varepsilon^{\eta} \{3 - 2(\eta - P)\} - (3 + 2P)$ $\pm \left[\varepsilon^{\eta} \frac{2}{\sqrt{\pi}} \left\{ 3 - 2(\eta - P) \right\} \int_{0}^{\sqrt{\eta}} \varepsilon^{-z^2} dz - 2\sqrt{\frac{\eta}{\pi}} (3 + 2P) \right]. (5)$

Equation (4) clearly shows that the potential which is established is the net contribution of both types of particles. Employing the notation

 $\left(\frac{d\eta}{d\xi}\right)^{2} = \phi(\eta) ;$ $\xi = \int_{0}^{\eta} \frac{d\eta}{\pm \sqrt{\phi(\eta)}}, \qquad (7)$

or

where the positive sign refers to β -region and the negative sign to α -region.

Solving equation (7) for large values of η we obtain as explained in paper I

$$\xi^2 = \frac{4}{9} \frac{\pi^{1/2}}{1+P} \left[\frac{e(V-V_m)}{kT} \right]^{3/2}, \qquad (8)$$

which with the help of (6) yields

$$i = \frac{\sqrt{2}}{9\pi} \frac{\left(\frac{n_e}{\sqrt{m_e}} + \frac{n_i}{\sqrt{m_i}}\right) \sqrt{e}}{n_e + n_i} \frac{(V - V_m)^{3/2}}{(x - x_m)^2}. \quad A \quad . \quad . \quad (9)$$

Thus if we neglect V_m and x_m for large values of V and plot i^2l^3 against V, the slope is given by

$$\left[\frac{\sqrt{2}}{9\pi} \frac{\left(\frac{n_e}{\sqrt{m_e}} + \frac{n_i}{\sqrt{m_i}}\right)\sqrt{e}}{n_e + n_i} \frac{A}{x^2}\right]^{2/3}$$

This evidently shows that the effective value of e/m for the mixture of particles is given by

$$\left[\frac{e}{m}\right]^{1/2} = \frac{\sqrt{e\left(\frac{n_e}{\sqrt{m_e}} + \frac{n_i}{\sqrt{m_i}}\right)}}{n_e + n_i}.$$
 (10)

Hence

$$\frac{n_i}{n_e} = \frac{\sqrt{m_e - \sqrt{m}}}{\sqrt{m} - \sqrt{m_i}} \sqrt{\frac{m_i}{m_e}}.$$
 (11)

In this particular experiment there seems to be a possibility of the existence of Li⁻ in the beam since Li atoms have a positive, though small, electron affinity. We shall, therefore, examine the possibility that there may be heavier Li⁻ ions mixed with the electrons in the inter-electrode space. The electron affinity of Lithium has been estimated by Glockler (1934) by an emperical extrapolation to be 0.34 eV and by Ta You Wu (1935) to be 0.54 eV. Assuming the very rough value of one volt we can calculate $\frac{n_i}{n_e} = \frac{p_i}{p_e}$ from the equation

$$\log K = \log \frac{p_a \times p_e}{p_i} = -\frac{E_f}{4.573 T} + \frac{5}{2} \log T - 6.479 + \log \frac{g_a \times g_e}{g_i},$$

where the pressures are expressed in atmospheres and $g_a=2$, $g_e=2$ and $g_i=1$, and E_f stands for the electron affinity of Li. Substituting the value T=1825°K, log $p_a=2.877$ (p_a being expressed in mm.), we obtain

$$\frac{n_i}{n_e} = \frac{1}{3200}$$

while for $E_f < 1$ volt this ratio will be still smaller.

Equation (11) shows that for such small values of n_i/n_e the effective e/m will not differ appreciably from its value for the electrons. Hence the low value of e/m obtained above from the slope is evidently due to the simple theory of unipolar current not being applicable to this case of mixture of particles of opposite charge. Incidentally these calculations show that the space charge method of

determining the electron affinity from the observed value of e/m as employed by Glockler (1935) is not sensitive enough to detect small electron affinities.

The positive particles, even though they do not reach the Faraday cylinder, will certainly affect the space charge with the result that the net negative space charge produced by the negative carriers becomes decreased as if the effective charge of each negative carrier was less than its true value, giving thereby a low value of e/m. Another way of looking at the problem is this. At lower accelerating voltages (for electrons) the proportion of positive particles present in the beam is greater than at higher voltages and hence the electron space charge and the space charge limitation of the current is less at a lower voltage, i.e., the current at lower voltage is relatively less decreased by the space charge than at higher voltage. This will produce a decrease in the slope of the $i^{2/3}$ versus V curve from what should occur in a pure beam and will thus give a low value of e/m.

The observations given in column (3) of table I have also been plotted (curve II in Fig. 4) and e/m from its slope comes out to be 1.37×10^{15} e.s.u./gm., a value about 400 times smaller than that for the electron and about 30 times greater than that for lithium. This shows either that the beam now contains a much larger percentage of some heavier ion (possibly Li⁻), or that there is a greater disturbing effect by the positive particles due to the increase in its relative proportion, but most probably it is due to a combination of both these causes.

III. THERMAL IONIZATION OF LITHIUM.

Experimentally the problem is similar to that of sodium except that due to the higher ionization potential and low vapour pressure of lithium the side furnace had to be modified. After some trials a side furnace of suitable size was designed in which sufficient vapour pressure could be developed to produce measurable ionization current.

The values of the vapour pressure of lithium at different temperatures were taken from those given by Bhatnagar (1943 b). The terms b(T) and b'(T) occurring in the ionization formula

$$\ln \frac{p_i \times p_e}{p_a} = -\frac{\chi}{kT} + \frac{5}{2} \ln T + \ln \frac{g_e(2\pi m_e)^{3/2} k^{5/2}}{h^3} - \ln b(T) + \ln b'(T), \dots (12)$$

are 2.000 and 1.000 respectively and hence formula (12) simplifies to

$$\log K = \log \frac{p_i \times p_e}{p_a} = -\frac{U}{4.573T} + \frac{5}{2} \log T - 6.479, \qquad (13)$$

where the pressures are expressed in atmospheres.

The equilibrium constant K is given experimentally by the relation

$$K = \frac{2\pi kT}{e^2S^2} \cdot \left(\frac{r^2 + d^2}{r^2}\right)^2 \frac{ig^+ig^-}{p_a} \frac{\sqrt{m_i \times m_e}}{(1.013 \times 10^6)^2}.$$
 (14)

With the aid of (13) and (14) the ionization energy U has been calculated. The currents i_g^+ and i_g^- occurring in equation (14) are the zero field values of the current obtained by measuring the saturation current at 5, 6, 7 and 8 volts and extrapolating these values graphically to zero field.

All the necessary data are given in Table II. It is found that the mean value for the energy of ionization comes out to be 123.4 K. cals. which agrees closely with the spectroscopically determined value 123.1 K cals.

TABLE II.

Diameter of the effusion hole = 1.71 m.m.,, ,, limiting diaphragm = 8.4 m.m.Current sensitivity of the galvanometer = 1.25×10^{-9} amp./mm. Distance between the effusion hole and the limiting diaphragm

=20.2 m.m.

			<u> </u>			1
Temp. of Graphite furnace °K	Temp. of Aux. furnace °K	$\log p_a$ in mm	ig Deflection in mm	ig ⁺ Deflec- tion in mm	log K atmos.	U in K
1768	858	2.6053	3600	45	1 4 ·4987	122.4
1783	873	2.7563	5800	68	14·6686	122.1
1823	871	2.7422	6800	83	$\widehat{14} \cdot 9172$	123.0
1828	886	2̄⋅8870	9500	108	13.0331	122.4
1863	900	1-0362	12000	127	13.0630	124.5
1888	903	Ĩ·0418	15000	179	13·3003	124.5
1909	915	1.2007	17100	177	13.3680	125.0
	1	<u> </u>				1.00

Mean = 123.4

SUMMARY

The apparatus already employed by us in the earlier experiments has been used to investigate the thermal ionization of lithium. The effusion currents have been measured with and without the magnetic field at various accelerating voltages for both positive and negative particles. The space charge theory developed in a previous paper for unipolar currents has been applied to the experimental data on the positive current under magnetic field. The value of e/m for the positive particle has been thereby determined. The magnetic field deflects the electrons and, with the assistance of the electrostatic field, makes the beam

effectively unipolar. An approximate theory has been developed for the case of a mixture of two types of particles of similar charge but different masses and the results have been tentatively applied to the negative currents. Calculations show that the simple unipolar theory for a bicomponent mixture as developed here is not applicable to the negative currents. The saturation currents are also measured and the energy of ionization of Li determined with the help of the ionization formula. The ionization potential comes out to be 5.35 volts, and the value of e/m for Li⁺ is found to be 3.3×10^{13} e.s.u/gm in fair agreement with the known values.

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